Sintering of Porous Silver Compacts at Controlled Heating Rates in Oxygen or Argon

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ABSTRACT

Submicronic (~0.4µm grain size) spherical silver particles were pressed into pellets and pre-fired at 235°C for 4 hours in static air. These porous silver compacts were densified in a dilatometer at heating rates (hr) of 2, 4 and 10°C min⁻¹ (up to ~ 600°C) under Ar or O₂. The total lineal densification ranged from 8 to 12% giving bodies of relative density ρ~0.80. After a small densification (stage (i)) each curve showed a clear Tᵈ (°C) at which the densification (AD(T)) exhibited a rapid increase (jump; stage (ii)), and had a characteristic peak in densification rate (DR(T)). Then the AD continued by another mechanism (stage (iii)), related to grain growth, till the densification rate started to decrease probably due to densification (stage (iv)) of closed pores located at 4-grain corners. For every atmosphere the Tᵈ increased with heating rate, and the Tᵈ values for O₂ were 79-105°C lower than those for Ar. From DR kinetics analysis it is concluded that under O₂ stage (ii) is due to grain boundary diffusivity (gb) whereas for stage (iii) the volume (vol) diffusion is the main process. From detail densification fits it is shown for stage (iii) there is an initial contribution to densification coming up from an initial stage controlled by (gb) diffusion, and that the main process is still the intermediate stage with simultaneous grain growth controlled by volume self-diffusivity.

For the Ar case the whole densification range appears to be controlled by (gb) diffusivity. Some impurity contamination of the Ag could produce a (gb) contamination under Ar gas such as for stage (iii) the controlling mechanism could become the (gb) process instead of volume diffusion.

Keywords: silver, solid state sintering and grain growth, surface tension, surface / grain boundary / volume- self-diffusions

1. INTRODUCTION

The sintering of silver particles has been extensively considered to test diffusional neck formation and densification theories [1-5]. For pure Ag are available nearly complete thermodynamic and self-diffusion data [4, 5, 7]. Nearly pure Ag and Ag / Pd-alloys powders are increasingly used for, respectively, terminating electrodes and internal electrodes (for barium titanate-based dielectrics) in multilayer ceramic capacitors [6]. The sintered structure of such terminating metal layer controls the thermal shock resistance of the capacitor-chip during wave soldering. For the second case efforts are directed towards an adequate co-sintering of the conducting inner electrodes with the ceramic layers to minimize the important problem of delamination.

For particle sizes smaller than about 1-2µm silver particles sinter faster under O₂ as compared to densification in vacuum or under inert gases like argon. Such behaviour was tentatively assigned to greater surface and grain boundary diffusivities [2,3]. In this work are measured the absolute linear densification (AD) and calculated the densification rates (DR) of pre-fired pellets (at 235°C in air) made of submicronic Ag particles. The sintering runs were made in a differential dilatometer at various heating rates under flowing O₂ or Ar gases. The objective of the work is to clarify how the surface (sd), grain boundary (gb) and volume (vol) diffusion mechanisms may control the sintering and grain growth kinetics.
2. EXPERIMENTAL

An experimental submicronic (~0.3-0.6µm grain size) spherical silver powder (SP) was mixed with 2wt% PVB [Poly (vinylbutyral), MW 150000, cat.#06100, Polysciences Inc., USA] and pressed into pellets (body A) of relative density (pr) close to 0.54%. The pellets were given a heat treatment at 235°C for 4 hours (body B) in static air, after which the pr values were increased by ~1-2%. The pre-heated pellets (B) were densified in a vertical differential dilatometer (Theta Inc., USA), fitted with a silica head, at heating rates (hr) of 2, 4 and 10°C min\(^{-1}\) under Ar or O\(_2\) pure atmospheres. The lineal densification \(\Delta l(T)/lo (=AD)\) was calculated from \(\Delta l(T)=lo-l(T)\), with \(l(T)\) the instantaneous thickness and \(lo\) the initial thickness of the pellet. The microstructure was studied in a scanning electron microscope (SEM, Philips 515) using fracture surfaces of the pellets before and after sintering.

3. RESULTS AND DISCUSSION

In Figure 1 is shown a typical micrograph of the fracture surface of preheated pellets (235°C for 4 hours). The submicronic particle size of Ag-SP is clearly seen and the particle agglomerates are quite uniform in size. In these pre-fired bodies the larger as well as the smaller pores are apparently uniformly distributed. The main densification and grain growth behaviours as well as some kinetics analysis are described next.

![Figure 1](image)

**Figure 1** – Fracture surface of a silver pellet pre-fired at 235°C for 4 hr under static air.

3.1. Densification behaviour

3.1.1. Absolute linear densification (AD(T)) and densification rates (DR(T))

In Figure 2 are collected the absolute linear densification \([AD=\Delta l(T)/lo]\) data and the densification rates \([DR=d(\Delta l(T)/lo)/dT]\) for dilatometer runs at 2, 4 and 10°C min\(^{-1}\) (under O\(_2\) or Ar flow). The end points in densification varied from \(AD_f\approx 0.08\) for \((AD(10), Ar)\) to \(AD_f\approx 0.12\) for \((AD(10), O_2)\). It is relevant to note the existence of well defined temperatures (Ti) for the onset of the major densifications. The Ti’s values are 294 (AD(2), O\(_2\)), 312 (AD(4), O\(_2\)), 340 (AD(10), O\(_2\)), 373 (AD(2), Ar), 417 (AD(4), Ar) and 444°C (AD(10), Ar). For increasing (hr) the Ti’s increased for both O\(_2\) and Ar, and, the Ti values for O\(_2\) were 79-105°C lower than those for Ar. The manner the curves shift towards higher temperatures, for (hr) increasing, differ significantly for both cases. For instance, with (hr) increasing the end point (D\(_{fr}\)) in densification increases for oxygen while it decreases for argon. The AD-curves show well defined densification regimes. Let us examine for example the run at 2°C min\(^{-1}\) under...
\( \text{O}_2 (\text{D}(2), \text{O}_2) \). There are the following regimes: (i) a small initial stage sintering [amounting to \( \text{AD}=0.002 \) at \(-294^\circ\text{C}\)], (ii) a strong densification jump [from 0.002 to 0.022 (at 309\(^\circ\text{C}\))], (iii) a steady densification [from 0.022 (309\(^\circ\text{C}\)) to 0.092 (427\(^\circ\text{C}\))], and (iv) a final slower densification [from \( \text{AD}=0.092 \) (427\(^\circ\text{C}\)) to \( \text{AD}=0.104 \) (567\(^\circ\text{C}\))]. These sintering regions may be assigned to the initial stage in solid state (SSS) sintering (i), to an unknown effect (ii), and to mainly grain growth controlled sintering for connected porosity (iii) and isolated porosity (iv) \([1, 4-6, 8-10, 12]\).

**Figure 2** – Densification (AD, top graph) and densification rate (DR) curves for specimens (B) heated at 2, 4 and 10\(^\circ\text{C} \text{ min}^{-1}\) under \( \text{O}_2 \) and \( \text{Ar} \).
3.1.2 Polycrystalline grain growth

In Figures 3 and 4 are shown the SEM micrographs corresponding to the final microstructures for runs performed at 10°C min⁻¹ under O₂ (AD(10),O₂) or Ar (AD(10),Ar). In relation to grain growth simultaneously with the removal of porosity, it should be noted after reaching the end points (ADf), every system showed uniform normal grain growth behaviour [8].

![Figure 3](image)

**Figure 3** – Fracture surface of the specimen sintered in the dilatometer at 10°Cmin⁻¹ under O₂.

![Figure 4](image)

**Figure 4** – Fracture surface of the specimen sintered in the dilatometer at 10°Cmin⁻¹ under Ar.
The final grain sizes $G_f$ (at $A_{D_f}$) were: 2-4 $\mu$m ($A_{D(2)}$, $O_2$), 3-5 $\mu$m ($A_{D(4)}$, $O_2$), 4-7 $\mu$m ($A_{D(10)}$, $O_2$), 1-3 $\mu$m ($A_{D(2)}$, Ar), 1-2 $\mu$m ($A_{D(4)}$, Ar), and ~3 $\mu$m ($A_{D(10)}$, Ar). It is first noted for a given atmosphere the grain sizes are quite similar. Secondly, the final grain sizes for $O_2$ are clearly larger than those corresponding to Ar atmosphere. It is important to notice no abnormal or secondary grain growth (characterized by large grains trapping porosity) was detected after these runs.

3.2. Kinetic analysis.

It is of interest to explain the very important differences in densification of these similar porous Ag skeletons by changing the heating rate (hr) and the sintering atmospheres. Here we present preliminary interpretations based on overall CHR (controlled heating rate) kinetics analysis (section 3.2.1), and, standard CHR equations for the initial and intermediate stages (section 3.2.2) in solid state sintering

3.2.1. Controlled heating rate estimation of sintering activation energies.

As discussed in [11] the isothermal densification in SSS controlled by self diffusion may be described by equation (1), such as

$$k(T) = (A \cdot D \cdot \gamma / G^\alpha \cdot T) \exp(-Q/RT) \cdot (\Delta l/l_0)^n = (AD)^n = k(T) \cdot t \cdot (1)$$

Do and Q are the pre-exponential factor and activation enthalpy of the self diffusion coefficient, $\Omega$ and $\gamma$ are the atomic volume and surface free energy, $G^\alpha$ is the grain size, T and R are the absolute temperature and gas constant, and $t$ is the densification time. The parameters $A$, $\alpha$, and $n$ depend on the particle shape.

For controlled heating rate CHR densification conditions, from the above equation (1), it may be derived the following logarithmic expression (2).

$$\ln [T \cdot (hr) \cdot (dD/dT)] = -(Q/R) \cdot (1/T) + \ln (A \cdot D \cdot \Omega \cdot \gamma) + \ln (G^\alpha) + \ln ((AD)^{1-n}/n) \cdot (2)$$

If the second and third terms in equation (2) do not change with temperature, the $Q$ value can be calculated if equation (2) is evaluated at the temperatures and $DR (=d(AD)/dT)$ values corresponding to constant shrinkage ($AD$) values. In Figure 5 are shown the clearly linear plots, for the $O_2$ runs, according to equation (2). For every O$_2$ system, an approximately similar grain size was assumed during densification (as noted in the previous section 3.1.2. where the grain sizes were considered).

The set of three values (for 2, 4 and 10°C/min$^{-1}$) was evaluated at: (1) the temperature of the maximum in DR curves (Figure 2), (2) the temperature of the end of the peak in DR, and (3,4) the temperatures for which the absolute densifications were $AD=0.06$ and $AD=0.08$. The latter being located well inside the region (iii) accounting for the greater densification extent. For the values corresponding to both the DR peak maximum and at its end, the apparent activation energies $Q$ were 118.7 and 99.1 kJoule mole$^{-1}$, respectively. These are roughly close to the value for the grain boundary (gb) self-diffusion in Ag of $Q_{gb}=84.4$ kJmole$^{-1}$ [7]. In contrast, for $AD=0.06$ and $AD=0.08$ the $Q$ values were 171.8 and 171 kJmole$^{-1}$, respectively, being close to $Q_v=192.1$ kJmole$^{-1}$, the activation enthalpy for lattice (vol) self-diffusion as determined in reference [7].

![Figure 5 – ln(T(K)*(hr)*DR) versus (1/T(K)) for pellets (B) heated at 2-10°C min$^{-1}$ under O$_2$.](image-url)

For the argon case, the plots were not linear. Even though, we have roughly estimated for the equivalent (1), (2) and (3), (4) temperatures, values of 84.4 kJmole\(^{-1}\) (DR-peak maximum), 96.4 kJmole\(^{-1}\) (end of DR peak), 113.3 kJmole\(^{-1}\) (AD=0.06) and 82.8 kJmole\(^{-1}\) (AD=0.07). These values for Ar case are roughly close to Qgb.

In [4,5] was found that for the sintering of spherical Ag powder in the intermediate stage, the experimental shrinkage rates for an argon atmosphere were lower than those for air atmosphere. It was advanced that at temperatures around 900°C (much higher than for the present cases) and for larger Ag particles (20-27µm in diameter) the considerably lower measured densification rates (under Ar) as compared to the values predicted from theory, could be related to impurities in the Ag particles. Such contamination would have decreased the surface energy significantly.

Summarizing, the above Q-values suggest that under O\(_2\) these pellets sinter during the last part of stage (ii) by the (gb) process, while for stage (iii) the volume self-diffusion appears to control the densification.

For the argon case, it appears that the (gb) diffusion is the dominating process for nearly the whole of the densification curve.

Therefore, for the O\(_2\) case, the clean grain boundaries would allow the volume diffusion to become the rate controlling process.

3.2.2. Specific sintering models for the initial and intermediate stages.

The much lower Ti values measured for O\(_2\) gas as compared to that for the Ar-case (see Figure 2) may be related to an enhanced (gb) self-diffusivity under O\(_2\) [2,3]. This would produce clearly lower temperatures for the start in densification via the initial stage either governed by (gb) diffusion or by (vol) diffusivity [5,7,10,12].

These AD shifts to lower temperatures for the O\(_2\) case could also be related to enhanced surface diffusivity for O\(_2\). In this way the dihedral stable angle (ψ\(_{SS}\); such as 2ψ\(_{SS}\) cos(ψ\(_{SS}\)/2) = γ\(_{SS}\); [γ\(_{SS}\)>γ\(_{GB}\) ] may be more quickly maintained at equilibrium facilitating the growth of the neck with densification. This would also favour the shifts in Ti values towards lower temperatures for the O\(_2\) runs. If the Ag particles heated under Ar are contaminated with impurities (in solid solution and/or at the surfaces), it could be expected lower (gb) and surface diffusivities. This would impede achieving the equilibrium ψ for which the sintering driving force is expected to reach its maximum value.

In [9,12] are presented logarithmic relationships for CHR conditions for the initial stage in SSS. For this stage one expects neck formation and neck growth with sintering up to about 2-5% linear densification. We applied such equations for (gb) or (vol) diffusion to the sintering curve for the run at 2°Cmin\(^{-1}\) under O\(_2\) flow [AD(2),O\(_2\)]. For the (i) stage, where indeed very little densification was measured, both models tend to give apparent Q values higher than those for Qgb or Qv. During such stage it is also expected that the surface diffusivity operates in these systems. The interesting point is that the model for (gb) diffusion fitted quite well the [AD(2), O\(_2\)]-values from 303 to 367°C, a temperature range extending from the jump (ii) up to the middle of the stage (iii) in densification (see Figure 2). That is, for the 303-367°C range and from the slope of the plot: ln(T°K) AD(T)\(^{0.56}\) DR(T) versus 1/T°K (see [9,12]), the obtained Q~ 86.9 kJ/mol is very close to Qgb.

The jump in densification (ii) could not be fitted to the above models nor to the intermediate stage Coble model [8]. The latter model is plotted in Figure 6 and for the temperature range covering the jump the apparent Q would be too high to have a reasonable physical meaning according to the diffusional models considered.

The reason for such a large increase in DR (at the corresponding Ti temperature, stage (ii)), could be related to densification via plastic flow of the porous silver skeleton.

For range (iii) it would be expected the intermediate stage in SSS to apply. In such a process densification occurs simultaneously with grain growth [8,12], such as the removal of porosity (P = 1-pr) in isothermal conditions could be approximated by equation (3); where D(T) is the sintering diffusion coefficient, and G(t,T) is the grain size.

\[-dP/dT = (10 D(T) \Omega \gamma / G(\gamma, T, kT))\] (3)

Assuming the grain size kinetics may be approximated by: \(G(\gamma, T, kT) = t Do \exp (-Qv/RT)\), and inserting t(hr)=T, then the plot:

\[W = \ln [T^2 (-dP(T)/dT) Do \exp (-Qv/RT)] \text{ versus } 1/(T°K)\]

should be linear, and from the slope the value for Qv should be recovered [that is, it may be assumed D(T)\(x\) \(\exp (-Qv/RT)\) for the oxygen case]. For isotropic densification, \(P(T) = (1- ((Lo/Lf)^2/(1-AD(T))^2))\), where (Lo, Lf) are the initial and final heights of the pellet. Then, \(dP/dT=-3 (L_f/Lo)^3 (d(AD)/dT) (1/(1-AD)^2)\).

Indeed in Figure 6 can be noted the very good linear fit for the whole of stage (iii), and the Qv value was equal to 196.9 kJ/mol, quite close to Qv=192.1 kJ/mol as measured in [7].

Therefore, for the main (iii) stage, the grain growth intermediate stage, controlled by volume diffusivity, is found to operate mainly. Some small but definite contribution to densification by (gb) controlled initial stage is also noted.

However, to fully check this approach via equation (3) the cubic law for grain growth:
G^3(t,T) = t Do exp (-Qv/RT) should be measured for the present Ag skeletons. These experiments will be attempted in the near future.

![Figure 6](image-url) – AD and W versus (1/T(ºK)) for the pellet heated at 2ºC min⁻¹ under O₂ flow.

CONCLUSIONS

Very porous silver skeletons (relative density (ρr) of 54-56%) were densified in a vertical differential dilatometer, fitted with a silica head, at heating rates (hr) of 2, 4 and 10ºC min⁻¹ under Ar or O₂ pure atmospheres. The porous pellets were made of spherical submicronic powder, ~0.4 mm in diameter. The total lineal densification [∆l(T)/lo] varied significantly upon changing either the (hr) or the atmosphere. It ranged from 8 to 12%, giving still porous bodies of ρr~0.80.

After a small initial densification (stage (i)) each curve showed a clear Ti (ºC) at which the densification (AD(T)) exhibited a rapid increase (jump; stage (ii)), and had a characteristic peak in densification rate (DR(T)). Then the densification continued via the intermediate stage mechanism (stage (iii)), related to grain growth, till the densification rate started to decrease probably due to densification (stage (iv)) of closed pores.

For every atmosphere the Ti increased with heating rate, and the Ti values for O₂ were 79-105ºC lower than those for Ar.

From DR kinetics analysis it is concluded that under O₂ stage (ii) is due to grain boundary diffusivity (gb) whereas for stage (iii) the volume (vol) diffusion is the main process. From detail densification fits it is shown for stage (iii) there is an initial contribution to densification coming up from an initial stage controlled by (gb) diffusion, and that the main process is still the intermediate stage with simultaneous grain growth controlled by volume self-diffusivity.

For the Ar case the whole densification range appears to be controlled by (gb) diffusivity. Some impurity contamination of the Ag could produce a (gb) contamination under Ar gas such as for stage (iii) the controlling mechanism could become the (gb) process instead of volume diffusion.

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